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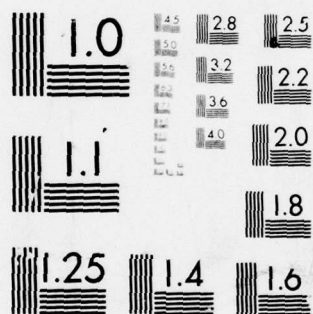
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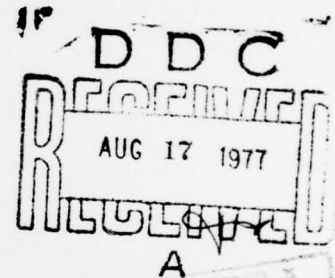
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EUROPEAN SCIENTIFIC NOTES

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PHYSICS
Absence of Radioactivity in Natural Rhenium Page
30

CHEMISTRY
Discussion on Unimolecular Reactions 31
Ionic Equilibria in Flames 33
The Hydrolysis of Triphenylbenzoic Esters 35
Friction and Lubrication 36
 Reflection Electron Microscopy of Surfaces 36
 Friction of Non-metals 36
 Boundary Lubrication 38

HYDRODYNAMICS
MGF (Multi-Glide-Surface) Bearings 38

BIOSCIENCES
Action of Cation-Exchange Resins in the Small and
 Large Intestines 39
Electrolyte Excretion in Experimental Potassium
 Depletion 40
Effects of Continuous Massive Alkali Administration
 in Man 40

MISCELLANEOUS
Technical Reports of ONRL 41

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ABSENCE OF RADIOACTIVITY IN NATURAL RHENIUM

From the energetics of beta decay one concludes that the existence of two neighboring isobars which are completely stable with respect to disintegration of one into the other is extremely unlikely. The radioactive transformation has been observed in the cases $A^{40} K^{40} Ca^{40}$, $Rb^{87} Sr^{87}$, $In^{115} Sn^{115}$, $Ba^{138} La^{138}$, and $Y^{176} Lu^{176} Hf^{176}$, but not in the cases $Cd^{113} In^{113}$ and $Sb^{123} Te^{123}$. The isobaric pair $Re^{187} Os^{187}$ has been investigated by Nalderett and Libby (Phys. Rev. 73, 487 (1948)) and by Sugarman and Richter (Phys. Rev. 73, 1411 (1948)). These investigators found a natural radioactivity associated with rhenium of about 4×10^{12} years and with an absorption curve corresponding to a β^- transition of energy 43 ± 6 kev. No activity was found in osmium. A preliminary report given at the Amsterdam Conference on Beta and Gamma Radioactivity in September, 1952, by D. Dixon, A. McNair, and S. C. Curran (Physica 18, 1161 (1952)) indicated that natural rhenium was radioactive but with a β^- transition of about 400 kev. These latter investigators at the University of Glasgow have greatly improved their technique and background since that time, and they now find no evidence for radioactivity in natural rhenium. They conclude that if it exists it must have a half-life of greater than 10^{16} years.

Dr. Curran and his collaborators at Glasgow make use of the proportional counter technique which they have

developed so extensively. The particular instrument involved in these measurements has a $5\frac{1}{2}$ -inch inside diameter and a 12-inch active length and is filled with four atmospheres of argon and 6 cm of CH_4 . It is operated at 5000 volts and is surrounded by a double bank of long Geiger counters arranged in anticoincidence with it. The sensitive area available for a sample is 1200 cm^2 . When surrounded by 4 inches of lead and placed underground, the background is found to be only 15 counts per minute. The initial counting rate with a rhenium sample was found to be due to the aluminum backing which was present. It is not known what element in the aluminum gave this high counting rate, but when the rhenium was backed with steel the counting rate was found to be much lower and in fact statistically equal to the background. When osmium was placed in the counter a very small activity was observed which gave pulses in the proportional counter of a size appropriate to osmium L X-rays. Curran and his co-workers believe that these are probably produced by gamma rays (principally from cosmic radiation) traversing the sample because similar X-rays, appropriate to the material, were observed when samples of platinum and tungsten were used. The rhenium sample was smaller in mass than the others so the effect was just barely observable in that case. These investigators conclude that there is no observable natural radioactivity in either rhenium or osmium and that the lifetime of any transition which occurs must be greater than 10^{16} years.

DISCUSSION ON UNIMOLECULAR REACTIONS

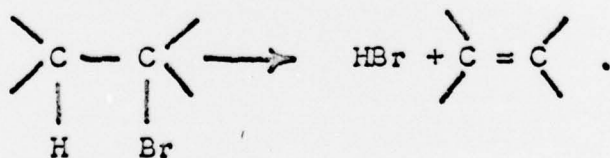
A half-day Discussion on Unimolecular Reactions was held in the Chemistry Department of University College, London, on 4 December 1953. The discussion was organized by Dr. Allan Maccoll and the introductory speaker was Dr. N. B. Slater (Leeds), whose recent theory represents a significant advance in this field. The discussion was most appropriate at this time, since during the past year Slater presented a rigorous theoretical treatment of the isomerization of cyclopropane; his curve reproduces extremely well the shape of the experimental pressure dependence of the rate down to 0.07 mm, while the absolute values are within a factor of 3.5 (cf. Proc. Roy. Soc. A217, 563; A218, 224 (1953)).

Slater's theory suggests that small molecules will show first-order kinetics only at impossibly high pressures, and the reacting molecule will have to contain six or more atoms to undergo a unimolecular reaction below 1 atmosphere. The observation reported by Dr. K. E. Hewlett (Bedford College, London) at this discussion, that, contrary to all previously-investigated reactions of this type, the dehydrochlorination of trichloroethylene appears to be second order, may provide additional support for this view. Since this molecule contains only six atoms the number of vibrational degrees of freedom within it is too small to permit significant unimolecular decomposition and thus the bimolecular reaction may become predominant.

One of the important possible advances remains the quantization of Slater's theory, and this development is being carried out at present by Dr. P. W. Higgs and Prof. H. C. Longuet-Higgins (King's College, London).

Dr. A. F. Trotman-Dickinson (Manchester; at present with Dupont, Niagara Falls) surveyed the known unimolecular reactions and reported some recent results from Manchester University. The decomposition of azomethane, one of the classical reactions of unimolecular kinetics, was reinvestigated using a toluene carrier gas technique and the results indicate that in the first step the molecule loses one methyl group (cf. J. Chem.Soc., 3878, 1953).

The unimolecular pyrolysis of alkyl bromides is being systematically studied by Dr. Maccoll; he finds that the pre-exponential term (the logarithm of the frequency factor) in the rate expression is only very slightly dependent on the nature of the carbon atoms involved, i.e., whether they are primary, secondary or tertiary. The reaction is of the general type

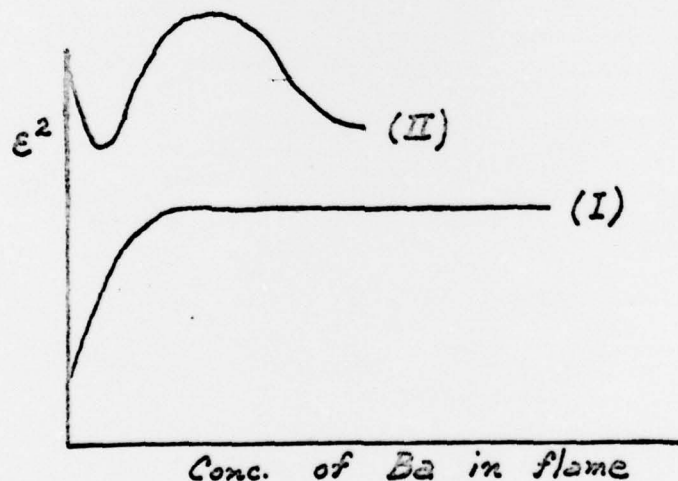


The dozen cases investigated so far include representatives of seven of the possible nine combinations, and their pre-exponential terms vary between 12.6 and 13.5.

A somewhat more detailed account of this discussion is given in Technical Report ONRL-142-53.

IONIC EQUILIBRIA IN FLAMES

In extending their work on ionic equilibria in flames containing metallic ions, Dr. T. M. Sugden and collaborators (Cambridge) have obtained some remarkable results in flames containing mixtures of alkali and alkaline earth metals. Using previously described techniques ((cf. Proc.Roy.Soc. A219, 204 (1953) and previous papers)) they investigated the change in electron concentration in the flame as a function of the relative concentration of alkaline earth metals. As a particular example the curves obtained for pure barium (I) and for barium containing 10 per cent cesium (II) are shown schematically in the figure below, where ϵ is a measure of the electron concentration.



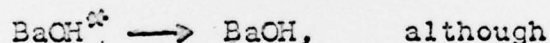
At lower Cs concentrations intermediate curves are obtained.

The results are interpreted by extending the concept of highly ionic molecular species in the vapor

phase; in these flames, species of the type BaOCs^+ and BaOH^+

are postulated. This concept of specific interactions in the gas phase leads to a consistent interpretation of the results; it is further substantiated by the fact that the effect of alkali metal addition on the electron concentration decreases in the order $\text{Cs} > \text{K} > \text{Na}$. This would be expected from both polarizability and size considerations. It should be noted, however, that the complicated curve shown above for the cesium-barium mixture can only be interpreted if one assumes that additional species, probably containing more than three atoms, are also present. Since the temperature prevalent in these hydrogen-air flames is not far above the condensation temperature of alkaline earth oxides, it is possible that nucleation is taking place, and one thus deals with growing species.

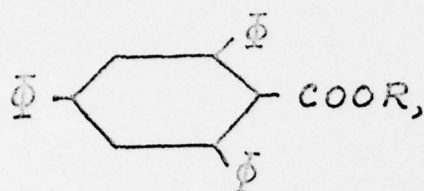
In addition to these microwave dielectric experiments, Sugden has also investigated regularities in the optical spectra of flames containing alkali and alkaline earth metals. Feeding alkaline earth metals to hydrogen-air flames (sometimes containing nitrogen), he observes two band systems; a diffuse band on the blue side of the sodium D line is interpreted as arising from the monohydroxides, BaOH , etc., and a sharp band system in the red as belonging to the oxides. The process giving rise to the diffuse band system, originating from an excited level, is probably



Species of the type $(\text{BaOH})^+$ are very stable and are again envisaged as highly ionic molecules best described as BaOH .

THE HYDROLYSIS OF TRIPHENYLBENZOIC ESTERS

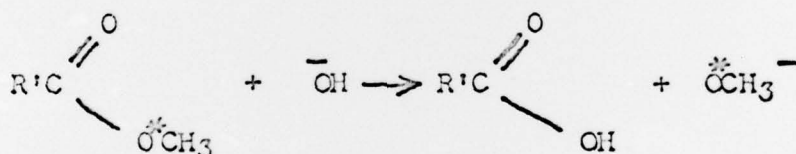
The hydrolysis of triphenylbenzoic esters, in different media repre-



sents a single system in which all known mechanisms of ester hydrolysis can be observed under suitable conditions (cf. C. K. Ingold, Structure and Mechanism in Organic

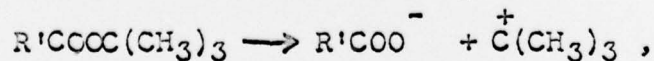
Chemistry, Cornell University Press, 1953, Table 47-1, p.754). Dr. C. A. Bunton (University College, London) has recently reviewed this field, discussing especially recent work at University College and at Bangor, Wales.

The mechanism of some of the reactions was elucidated using O18-enriched esters, and it appears that the outstanding remaining problem is to explain the observed difference in the hydrolysis of the methyl-ester in 95 per cent aq. methanol and in 70 per cent aq. dioxane. In dioxane the reaction occurs with acyl-oxygen fission



while in methanol no exchange occurs and alkyl-oxygen fission is probable. Small amounts of dimethylether may have been formed, but would be difficult to detect.

The tert.-butyl ester hydrolysis gives the normal acid in both dioxane and methanol. (At higher temperatures, > 120°C in aq. dioxane considerable dehydration resulting in isobutylene formation was noted.) In contrast with the simpler, CH₃, C₂H₅, etc., esters, the tert.-butylester hydrolyzes rapidly and according to first-order kinetics. The first step is



and this is not sterically hindered by the phenyl groups in R'.

FRICTION AND LUBRICATION

The laboratory for the Physics and Chemistry of Surfaces directed by Dr. F. P. Bowden, which forms part of the Department of Physical Chemistry at Cambridge University, has a well-diversified research program on the fundamental mechanisms of surface phenomena, including friction and lubrication. Bowden's chief collaborator in these activities is Dr. D. Tabor, and their book, The Friction and Lubrication of Solids, Oxford University Press, 1950, described the work of the laboratory up to 1949; a revised second version of this monograph will appear during 1954.

The friction of non-metals and the mechanism of boundary lubrication are the two fields in which the largest body of interesting new results have been accumulated since the publication of the monograph mentioned above. Some of these results are discussed below. Further details about the work of this laboratory can be found in Technical Report ONRL-1-54.

Reflection Electron Microscopy of Surfaces

Among the various recent techniques, Dr. J. W. Menter's development of reflection electron microscopy of surfaces at small glancing angles is noteworthy. The electron gun of a conventional Metropolitan-Vickers instrument is tilted a few degrees away from its usual vertical position and the scattered electrons are collected and focused to provide an image of the surface. In view of the scattering losses, the considerable reduction in the maximum enlarging power must be accepted. This is outweighed, however, by the advantage gained through the avoidance of the use of replicas, and it thus is possible to follow surface changes directly in the electron microscope. At a recent Discussion on Combustion in Cambridge, Bowden showed some preliminary observations on a decomposing silver azide surface on which individual decomposing regions could be clearly distinguished.

Friction of Non-metals

The results of a large amount of work on the friction of non-metals suggest that an adhesion mechanism similar to that suggested for the friction of

metals applies here also. In a detailed study of the strength and friction of crystalline rocksalt, Dr. R. King found that the specific shear strength of this material in the contact region is nearly ten times as great as the bulk shear strength of a rocksalt single crystal. The pointed corner of one rocksalt crystal is slid over the flat cleavage face of another in these experiments, and the width of the well-grooved track which is formed gives an approximate measure of the area of intimate contact between the sliding surfaces. The reason for the large shear strength observed is that under the high hydrostatic pressures operating in the region of contact, the material is no longer brittle and can undergo marked plastic deformation. This explanation is strikingly supported by compression experiments carried on between glass anvils in which two rocksalt specimens are welded together by direct compression. It was observed that the cracks which traverse the crystals during the early stages of the compression are healed as the pressure is increased, the flaws are closed by the high hydrostatic pressures, and the material becomes relatively ductile.

Multiple-beam interferometric techniques were used by Miss A. Bailey to study the interaction between sheets of mica which are molecularly smooth over an appreciable area. The mica sheets are bent into cylindrical form and two such cylinders are pressed together with their axes at right angles. The region of contact is examined interferometrically and the adhesive and tangential forces required to produce sliding are both measured. Preliminary results indicate that over clean surfaces the friction is extremely high and the shear strength of the contact region is of the order of 400 gm/mm^2 . In measurements of the adhesion between the surfaces it was found that the contact area does not drop to zero as the load is removed; a finite normal force is required to pull the surface apart, and the tensile strength of the contact region is of the same order of magnitude as the shear strength of the interface during sliding. The addition of a monolayer of soap produces a strikingly large reduction in the area of intimate contact and also, of course, in the friction and adhesion.

Boundary Lubrication

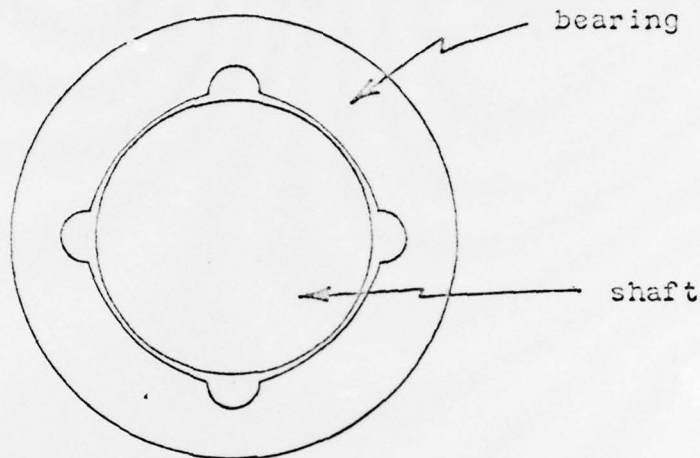
The available experimental results on the mechanism of boundary lubrication all confirm the view that the main function of a lubricant film is to reduce the amount of metallic interaction at those regions where the surfaces would otherwise form large metallic junctions and to inhibit the growth of junctions when sliding occurs. The lubricant film must also be easily sheared, and therefore long chain compounds are most suitable. The state of the lubricant film is also important. It is most effective when the film is in the solid state; an appreciable rise in friction occurs at the melting point of the lubricant film, but its remaining attachment to the surface suffices to reduce metallic friction by a factor of several hundreds. This protection persists until the lubricant film becomes mobile or is dissolved; once this stage is reached, it has practically no value.

MGF (MULTI-GLIDE-SURFACE) BEARINGS

A new type of hydrodynamic bearing has recently been invented by Dr. W. Frössel of the Max Planck Institut für Strömungsforschung, Göttingen. This bearing has been named the MGF Bearing, or Mehrgleitflächen-Lager. The usual cylindrical hydrodynamic bearing has the shape of the oil passage between the shaft and the bearing directly specified by the play in the bearing, and the shaft in a cylindrical bearing gets support against a lateral load only from one small region in the narrowest part of the oil passage. In Frössel's invention, the round bearing is replaced with one in which there are three or more sections, each of which has a shape designed to simulate any desired eccentricity, and between each of which lies an oil groove to guarantee a sufficient supply of lubricant. Each of the sections exerts a force on the shaft dependent on the position of the shaft, speed of rotation, and oil viscosity.

The general difference in behavior between a cylindrical bearing and an MGF bearing may be described by the statement that the behavior of an MGF bearing is much more linear. This is primarily due to the fact that the several surfaces have a strong centering action,

which also gives the bearing greater stability. It is claimed that the bearing is particularly suitable for very high rotational speeds, and that it is able to take high shock loads and to have relative freedom from noise. Tests have been and are being made at speeds above 33,000 rpm, with inexpensive bearing metals, and under shock loading.



This type of bearing was described in an article by W. Frössel, "Einige Eigenarten der hydrodynamischen Schmierung", Technische Mitteilungen 45, Heft 9/10, 1 (1952). The invention is being developed and exploited by the firm Gleitlager-Gesellschaft m.b.H., Weender Landstrasse 96-102, Göttingen, from whom technical information may be obtained.

ACTION OF CATION-EXCHANGE RESINS IN THE SMALL AND LARGE INTESTINES

Drs. A. G. Spencer and E. J. Ross of University College Hospital Medical School, London, studied the uptake of sodium and potassium ions by cation-exchange resins at different levels of the intestinal tract of rats. Sulphonated polystyrene was placed in isolated loops of the bowel. In some cases the resin contained tracer doses of Na^{24} or K^{42} , while in others radioactive material was injected intravenously and the resin was non-radioactive. Measurements of the cation content of

the resins were made at 30, 60 and 90 minutes after the commencement of the experiment. It was found that resin in the gut acts like an electrolyte compartment anywhere else in the body. The rates of cation exchange varied in different parts of the intestine, and the uptake of sodium from the resin to the blood stream and from the blood stream to the resin, depending upon the experimental conditions, was fast in the small intestine compared with the exchange of potassium at this level. This situation tends to be reversed in the large intestine.

When rats were placed on a low sodium diet, the mean daily excretion of cations in the stools was 5 meq. of sodium and 9 meq. of potassium. When the animals were maintained on a low sodium diet and resin was introduced into the intestine, the mean daily excretion of sodium in the stools increased to 28 meq. and the potassium increased to 70 meq.

ELECTROLYTE EXCRETION IN EXPERIMENTAL POTASSIUM DEPLETION

Drs. M. D. Milne, N. C. Hughes and B. M. Evans of the University of Manchester produced an experimental potassium depletion in human volunteers by feeding a low potassium diet over a 2-week period. The volunteers were then subjected to 5 types of stimuli which can normally be expected to cause increased urinary potassium loss ((1) hyperventilation, 2) osmotic diuresis produced by intravenous mannitol injections, 3) ingestion of sodium bicarbonate, 4) ingestion of carbonic anhydrase inhibitor (250 mg.), 5) ingestion of potassium salts (10 g. KCl)). Only a very slight urinary potassium loss was produced by these stimuli, indicating that when a potassium depletion exists there is an effective renal conservation of potassium. In addition, the normal diurnal rhythm of potassium excretion is simultaneously greatly reduced.

EFFECTS OF CONTINUOUS MASSIVE ALKALI ADMINISTRATION IN MAN

Drs. G.M.T. Van Goidsenhoven, O. V. Gray, A. V. Price and P. H. Sanderson of St. Mary's Hospital, Medical Unit, London, administered sodium bicarbonate in a continuous intragastric milk drip in doses up to 140 g. daily for 3 weeks to patients undergoing treatment for peptic

ulcer. A chemical alkalosis with blood pH. of 7.5 to 7.54 was produced, but there were no subjective symptoms referable to the treatment. There was no evidence of renal damage as determined by urea clearance and other renal function tests. During the alkali administration, large amounts of sodium (700 to 800 meq.) were retained. Inulin space determinations suggested that some 90 per cent of the sodium was held in the extracellular fluid.

TECHNICAL REPORTS OF ONRL

The following reports have been forwarded to ONR, Washington. Copies may be obtained by addressing requests to the Commanding Officer, Office of Naval Research Branch Office, Navy No. 100, c/o Fleet Post Office, New York, N. Y.

- ONRL-130-53 "Reactions Between Gases and Solids" by
G. J. Szasz
- ONRL-135-53 "The CERN Colloquium on the Strong Focus-
ing Proton Synchrotron" by J. R. Richardson
- ONRL-136-53 "Meeting of the European Section of the
International Union Against Cancer" by
J. L. Tullis and G. J. Szasz
- ONRL-137-53 "The Third Meeting of AGARD" by W. D. Hayes
- ONRL-138-53 "The Scottish Marine Biological Association"
by T. K. Ruebush
- ONRL-139-53 "Physical Research on Solids and Liquids in
Italy" by J. R. Reitz
- ONRL-140-53 "Laboratory Meeting of the Royal Society of
Tropical Medicine and Hygiene" by
T. K. Ruebush
- ONRL-141-53 "Physiological Society Meeting at King's
College, London" by J. L. Nickerson

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